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(54) Title: MICROPOROUS MEMBRANE WITH ADSORBENT MULTI-FUNCTIONAL FILLER

(57) Abstract: The invention relates to a microporous membrane that incorporates a polymeric-based resin and a multi-functional filler. The predominately activated carbon based filler serves a multi-functional purpose including acting as a mechanical pore forming agent, as well as providing a defined degree of chemical resistance by nature of its inherent adsorptive characteristics. The multi-functional microporous membrane exhibits breathability via moisture vapor transmission, resistance to particulate penetration, and resistance to chemical penetration and permeation. The unique membrane also exhibits characteristics of odor control.

## MICROPOROUS MEMBRANE WITH ADSORBENT MULTI-FUNCTIONAL FILLER

### FIELD OF INVENTION

This invention relates generally to microporous composite materials and to their method of manufacture, and more particularly to microporous composite 5 materials of the type that are useful in protective garments and other applications.

### BACKGROUND OF THE INVENTION

Numerous approaches have been undertaken to develop protective barriers and composites that offer resistance to defined hazards while still offering the wearer a certain degree of comfort. High degrees of chemical resistance to a wide 10 array of chemical hazards can be achieved using barrier materials in the form of air-impermeable continuous films and composites. However, protective clothing made of such barrier materials is uncomfortable, since the barrier material totally blocks the body's natural heat regulating ability. The expanded use of chemical protective clothing has pushed garment designers to explore alternative approaches 15 to balancing barrier and comfort.

One approach to producing "breathable" chemical barriers has been described in von Blucher et al. U.S. Pat. No. 4,677,019. This approach, as well as numerous other variants, combines traditional textiles, nonwovens, foams, etc., with activated carbon in multi-layered laminates. Activated carbon is widely used 20 as a sorptive media for the removal of impurities and/or gaseous species present in low concentration in liquid, air, and gas streams. Activated carbon is characterized by having high specific surface area (e.g., 300-2500 square meters per gram) by consisting of macropores (i.e., pores with diameters greater than 500 angstroms),

mesopores (i.e., pores of diameters 20-500 angstroms), and micropores (i.e., pores of a diameter less than 20 angstroms).

Activated carbon had been adapted for garment textile usage in various configurations such as described, for example, by Simpson U.S. Pat. No. 5 4,726,978, Goldberg U.S. Pat. No. 4,945,392, Katz U.S. Pat. No. 5,162,398, Sessleman U.S. Pat. No. 5,383,236, Stelzmuller et al. U.S. Pat. No. 5,731,065, Smolik U.S. Pat. No. 5,769,992, and Conkle et al. U. S. Statutory Invention Registration No. H823.

The major advantage of activated carbon is its affinity for a wide range of 10 chemical species. Its greatest disadvantages are ease of saturation to liquid exposure and durability of the adhered carbon. To avoid these limitations, manufacturers typically combine the activated carbon layer with an abrasion-resistant, liquid-repellent outer layer and an additional abrasion resistant inner layer. See Langston U.S. Pat. No. 5,112,666 and Collier et al. U.S. Pat. No. 15 5,453,314. The liquid-repellant finishes are typically surface treatments of silicones or Teflon® which provide run-off type performance but can still become saturated during heavy exposure to liquid challenges and can be easily overcome under pressure (i.e., hydrostatic pressure) such as can occur in the crutch of the arm and other high flex areas of a garment.

Several approaches have been made to develop strategies to avoid 20 saturating the adsorptive media contained in these products. Simpson U.S. Pat. No. 4,726,978, Nomi U.S. Pat. No. 5,190,806 and Kelly U.S. Pat. No. 5,273,814, as well as others, have combined various porous, microporous, and monolithic layers with sorptive or detoxifying media in multi-layer composites. While 25 functional, these complex structures are expensive, difficult to manufacture, and exhibit delicate field performance due to abrasion and adhesion issues of the sorptive media. Air-permeable outer layers are obviously preferred in garment applications since they will maximize wearer comfort. Microporous and monolithic layers offer no measurable airflow and thus must exhibit high rates of 30 moisture vapor transmission to be usable as garment materials. A major deficiency in the air permeable approach is that these composites are limited to vapor and airborne challenges. The air-impermeable approaches have typically relied on

monolithic films and coatings of polyurethane and polyester, or microporous films of sintered polytetrafluoroethylene (PTFE).

Microporous films comprised of polyolefins and polytetrafluoroethylenes are known in the art. Hoge U.S. Pat. No. 4,350,655, Sheth U.S. Pat. No. 5 4,777,073, Wu et al. U.S. Pat. No. 5,865,926, Soehngen et al. U.S. Pat. No. 4,257,997, Gillberg-LaForce U.S. Pat. No. 5,328,760, Nagou et al. U.S. Pat. No. 4,791,144, Jacoby U.S. Pat. No. 5,594,070, Gore U.S. Pat. No. 4,187,390, Weimer et al. U.S. Pat. No. 5,690,949, and others describe examples of coatings, films, membranes and composites that offer air impermeability, liquid resistance, and 10 high degrees of moisture vapor transmission through various microporous structures. Processes for producing the micropores vary and include cold rolling, and stretching (mono-axially, biaxially, and incrementally) filled films. For stretched films, the mechanism for cavitation can include a solid particle (i.e., calcium carbonate) that will remain in the film after stretching or a soluble 15 component (i.e., mineral oil) that can be extracted after stretching thus leaving the void.

Liquid-impermeability in microporous films is typically surface tension related and is controlled by the size and size distribution of the pores. The interconnection of the pores is the mechanism by which moisture vapor is 20 transported through the otherwise air-impermeable films. By themselves, these membranes are best suited for liquid and particulate challenges and are otherwise penetrated by vapor challenges as they are by water vapor molecules.

Additional attempts have been made to improve the moisture vapor transmission capacity of monolithic or permselective films by incorporating 25 various fillers that ideally disperse moisture via molecular diffusion through the adsorptive filler material such as described by Sikdar et al. U.S. Pat. No. 6,117,328. Moisture transport through these type films is limited by the fact that the filler material particles must be in direct contact with each other to provide a pathway for movement of the moisture. The chemical adsorption capacity of the 30 filler material is further limited by the fact that its entire surface which would otherwise be available for adsorption is encased in the base resin of the permselective film.

Permselective films such as those described by Nakao et al. U.S. Pat. No. 4,909,810, Baker et al. U.S. Pat. No. 4,943,475, Athayde et al. U.S. Pat. No. 5,024,594, Baurmeister U.S. Pat. No. 5,743,775, Blume et al. U.S. Pat. No. 5,085,776, and others are using ultra-thin films in various composites in protective clothing, as well as gas and liquid separation applications. With chemical diffusion based on Fick's Law and diffusion and solubility parameters, these thin films are designed to preferentially allow the transport of one or more chemical species through the film. Those permselective films that are best suited for garment applications such as described by Baurmeister are based on cellulosic resins to allow the transport of moisture, but are unfortunately degraded by a wide range of common industrial chemicals which limits their applicability.

#### SUMMARY OF THE INVENTION

The present invention addresses the above-mentioned deficiencies in sorptive fabrics, composites, and microporous films by disclosing a novel approach of combining the sorptive characteristics of activated carbon with the barrier properties of a microporous membrane, which translates to a simplified, high performance membrane, or composite that exhibits multiple attributes. The resultant membrane exhibits breathability via moisture vapor transmission, water and blood repellency, particulate penetration resistance, windproofness, odor adsorption and resistance to chemical penetration and permeation.

Calcium carbonate is the most common mechanical pore-forming agent used in the manufacture of microporous films and membranes. Its widespread use is based on its low cost, inertness, water insolubility, as well as ease of pulverization and processability. While other organic and inorganic mechanical pore forming agents have been considered such as clays, titanium oxide, siliceous fillers, barium sulfate, zeolites, etc., their use has been limited to functioning as a pore forming agent. The novelty of the present invention is to utilize a multi-functional mechanical pore-forming agent in place of the traditional mono-functional agents. The multi-functional agent of the present invention functions as a mechanical pore forming agent during manufacture of the membrane, and

thereafter remains in the membrane to function as a chemical and/or odor sorptive agent.

Wu, Sheth, Jacoby, Hoge, and others disclosing microporous processes based on mechanical pore forming agents such as calcium carbonate neither 5 disclose nor suggest utilizing multi-functional mechanical pore forming agents such as activated carbon that, when left in place within the pore after cavitation, serves the additional function of adsorbing chemical vapors, odors and/or liquid impurities passing through the film. This novel use of activated carbon improves and expands the usefulness of microporous films beyond their traditional 10 boundaries.

Performance characteristics in addition to those described above can be engineered into the membrane in several ways. Properties such as flame resistance, anti-static characteristics, thermal degradation resistance, UV resistance, degradability/compositibility, and other properties can be achieved 15 through various custom and commercially available additive packages. For example, in addition to the activated carbon, there can also be dispersed throughout the membrane at least one additive selected from the group consisting of flame retardants, anti-static additives, anti-microbial additives, antioxidants, stabilizers, UV absorbers, and enzyme additives. Morrison U.S. Pat. No. 4,343,853, for 20 example, describes various additives that can be incorporated into the membranes of the present invention to instill fungicidal and antibacterial characteristics, examples of which include nitrophenyl acetate, phenylhydrazine, polybrominated salicylanilides, chlorhexidine, domaphen bromide, cetylpyridinium chloride, benzethonium chloride, 2,2'-thiobisthiobis (4,6-dichloro)phenol, 2,2'- 25 methylenebis(3,4,6'-trichloro)phenol, 2,4,4'-trichloro-2'-hydroxydiphenyl ether, and or other similar anti-microbial agents of which Microban® is a commercially available example. Weimer et al. U.S. Pat. No. 5, 690,949 describe the use of fluoroochemical additives as a method of improving the repellency characteristics of microporous films, preferable are fluoroochemical oxazolidinone compounds and 30 fluorochemical amino-alcohol compounds, and amorphous fluoropolymer of which Teflon® is a commercial example.

The present invention can be embodied as an adsorbent microporous free film or membrane, or as a composite containing the microporous adsorbent film or membrane combined with one or more additional microporous membranes and/or layers of fabric, scrim, or supporting media. The free film/membrane or the  
5 composite, can be used as a protective covering or packaging, protective clothing item or liner, glove or liner, filter or filter component, separation membrane, or as an odor control device in personal hygiene products (i.e., feminine care products, diapers, etc.) or outdoor sports apparel (i.e., hunting apparel, etc.), or any other product or application requiring breathability, chemical and/or particulate  
10 resistance, and/or odor control.

#### BRIEF DESCRIPTION OF THE DRAWING

Having thus described the invention in general terms, reference will now be made to the accompanying drawings, which are not necessarily drawn to scale, and wherein:

15 Fig. 1 is a schematic perspective view showing an unsupported free film membrane according to the present invention; and

Figs. 2 to 6 are fragmentary perspective views showing a composites according to several embodiments the present invention.

#### DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

20 The present inventions now will be described more fully hereinafter with reference to the accompanying drawings, in which some, but not all embodiments of the invention are shown. Indeed, these inventions may be embodied in many different forms and should not be construed as limited to the embodiments set forth herein; rather, these embodiments are provided so that this disclosure will satisfy  
25 applicable legal requirements. Like numbers refer to like elements throughout.

Microporous membranes in accordance with the present invention are produced from a thermoplastic polymeric resin material that is capable of being heated to a molten or flowable state and extruded in the form of a substantially continuous film. Suitable polymeric resin materials may be selected from the  
30 group consisting of polyolefins, polyolefin copolymers, polyesters, polyamides,

polyvinyl alcohol, polycaprolactone, starch polymers, and blends of these materials. Particularly preferred polyolefin compositions include polypropylene, copolymers of propylene with ethylenically unsaturated monomers such as ethylene, high-density polyethylene, medium density polyethylene, and linear low density polyethylene.

The thermoplastic polymer resin material is blended with an activated carbon filler material. The amount of filler material present in the blend may be varied, depending upon the degree of porosity desired in the membrane.

Preferably, however, the filler constitutes at least 5% by weight, and for some applications preferably from 40 to 90 weight percent of the blend. The filler and the resin material are blended together to form a homogeneous mixture, either in a preliminary compounding step or directly in a suitable mixing extruder. The activated carbon filler material can be used as the sole filler material in the resin, or in certain applications it may be desirable to blend additional filler materials as mechanical pore-forming agents with the activated carbon filler material.

Examples of additional organic and/or inorganic mechanical pore-forming agent include zeolites, clay, calcium carbonate, barium sulfate, magnesium carbonate, magnesium sulfate, alkaline earth metals, baking soda, activated alumina, silica, calcium oxide, soda lime, titanium dioxide, aluminum hydroxide, ferrous hydroxides, diatomaceous earths, borax, acetyl salicylic acid, molecular sieves, ion exchange resins, talc, kaolin, silica, magnesium carbonate, barium carbonate, calcium sulfate, zinc oxide, calcium oxide, mica, glass, wood pulp, and pulp powder, and mixtures of the foregoing.

In addition, other additives can be incorporated into the membrane. For example, a starch additive can be dispersed throughout the membrane to promote degradation of the membrane when exposed to sunlight or other environmental influences. Other additives that can be blended with the polymer and activated carbon filler include flame retardants, anti-static additives, anti-microbial additives, antioxidants, stabilizers, UC absorbers, and enzymes.

The term "activated carbon" as used herein is a generic term describing a family of carbonaceous adsorbents with a highly crystalline form and extensively developed internal pore structure. A carbon substance is subjected to a controlled

oxidation process, called "activation", to develop its porous structure. The pores obtained offer a vast surface area capable of attracting an extensive number of molecules in liquid or gaseous phase through adsorption. The highly porous activated carbon may typically have surface areas of from about 300-2,500 square meters per gram. The greater the surface area, the higher the number of adsorptive sites available. These so-called active, or activated, carbons are widely used to adsorb various substances from gases or liquids. Various method are used to determine the activity level of activated carbon. The Iodine number provides a measurement of the porosity of an activated carbon by adsorption of iodine from solution. Standard test method ASTM D4607 can be used for measuring Iodine Number. Preferably, the activated carbon used in the present invention should have an Iodine Number of at least 900 mg/g. Carbon tetrachloride activity provides a measurement of the porosity of an activated carbon by the adsorption of saturated carbon tetrachloride vapor. The carbon tetrachloride activity on a weight basis can be determined using the ASTM standard test method D3467. Activated carbons for use in the present invention preferably have a carbon tetrachloride activity of 60 % or greater. Other test methods such as the butane test of ASTM method D5228 have also been devised for measuring the activity of activated carbon. The adsorption capacity of membranes in accordance with the present invention can be measured by adapting the industry standard tests, such as the carbon tetrachloride activity test of ASTM D3467, for a membrane material.

Activated carbons preferred for use in the present invention have a mean particle diameter less than 15 microns, more preferably less than 5 microns, and most desirably less than 1 micron (submicron). The mean particle diameter can be measured directly using laser measurement techniques. The activated carbon filler material can be treated with conventional surface modifiers to minimize agglomeration, improve dispersion and to facilitate obtaining high loading of the filler in the polymer material. For example stearates, such as calcium stearate, are conventionally used for this purpose.

The adsorbent microporous membrane of the present invention can take the form of an unsupported or "free" film, or the membrane can be combined with one or more other layers to form a microporous composite. The microporous

membrane or composite can be manufactured in accordance with any of a number of manufacturing processes known in the art for producing microporous films and composites, such as those described in the below-mentioned United States patents, the disclosures of which are hereby incorporated by reference.

- 5       For example, an unsupported microporous "free" film membrane , such as that indicated by the reference number 10 in Figure 1, can be produced generally in accordance with the teachings of Jacoby U.S. Pat. No. 5,594,070 by extruding a thermoplastic polymer composition containing activated carbon filler material and a beta-spherulite nucleating agent from a slot die to form a film, allowing the
- 10      extruded continuous film to cool and solidify, subjecting the film to an extracting step to extract beta-spherulites, and subsequently stretching the thus formed film uniaxially or biaxially, thereby producing a film having microscopic pores throughout. The microscopic pores impart breathability to the film. The activated charcoal filler remains present in the film in the vicinity of the microscopic pores
- 15      and thus imparts adsorbent properties to the microporous film membrane. Suitable adsorbent microporous membranes or films can also be produced without the extraction step. For example, following the teachings of the Hoge U.S. Pat. No. 4,350,655, a thermoplastic polymer composition blended with activated carbon in finely divided particulate form can be extruded from a slot die to form a film, and
- 20      can be subsequently stretched, with or without embossing, to form adsorbent microporous film membrane. Similarly, a process similar to that described in Sheth U.S. Pat. No. 4,777,073 can be utilized to form adsorbent microporous film membrane from a blend of polypropylene or polyethylene and activated carbon. In this process, a continuous film is extruded from a slot die and his subsequently
- 25      embossed with a pattern to embossing roller. The embossed film his subsequently cold stretched, imparting microporosity to the film.

- Unsupported or "free" films produced by any of the above noted processes can be used alone, or they can be combined with additional layers or supporting substrates. For example, a microporous film can be laminated to a nonwoven, knitted, woven or scrim substrate either with an adhesive or by direct fusion of the thermoplastic film membrane, such as for example by thermal point bonds. Figure

2 illustrates a composite material 11 in which an adsorbent microporous membrane 12 is laminated to a flexible scrim reinforcing substrate 13.

In yet another approach, a microporous adsorbent membrane material can be produced generally in accordance with the teachings of Weimer et al. U.S. Pat.

5 No. 5,690,949. In this process the thermoplastic polymer material is blended with a mineral oil in addition to the activated carbon filler. Upon cooling of the thermoplastic polymer composition, a phase separation occurs between the polymer compound and the processing oil.

In still another embodiment, illustrated in Figure 3, an adsorbent 10 microporous membrane composite material 14 can be produced by extrusion coating a film or layer 15 of a microporous formable composition containing a thermoplastic polymer and activated carbon filler onto a nonwoven fabric reinforcing substrate material 16, to form a continuous film on the reinforcing substrate. The film/nonwoven substrate composite 14 is subsequently stretched to 15 render the composite microporous. A process similar to that described in Wu et al. U.S. Pat. No. 5,865,926 can be suitably employed.

Figure 4 illustrates a multi-layer microporous composite material 20 that includes an outer microporous membrane layer 21 formed from a stretched calcium carbonate-filled polymer film laminated to an underlying adsorbent microporous 20 membrane layer 22 formed from a stretched activated carbon-filled polymer film 22 and adhered together by dots of an adhesive 23 applied in a open spaced pattern.

Figure 5 illustrates a tri-laminate microporous composite material 30 that includes a microporous membrane inner layer 31 containing thermoplastic polymer 25 and activated carbon filler, with an outer layer 32 laminated to the membrane by an adhesive (not shown) such as a hot melt adhesive or a polyurethane adhesive. A rear fabric layer 33 formed of a spunbond nonwoven fabric is laminated to the rear surface of the inner membrane layer 31.

Figure 6 illustrates a tri-laminate microporous composite material 40 that 30 includes an outer microporous membrane layer 41 formed from a stretched calcium carbonate-filled polymer film laminated to an underlying spunbond nonwoven fabric reinforcing layer 42, which in turn, is laminated to an adsorbent microporous

membrane layer 43 formed from a stretched activated carbon-filled polymer film. The layers are adhered together by adhesive (not shown) applied by spraying.

## EXAMPLES

5       The following embodiments of the disclosed invention demonstrate the potential breadth and significance of the present invention. Inclusion of these embodiments in no way serves to limit the potential breath and applicability of the present invention to other configurations and or uses.

### Example 1

10       A microporous, activated carbon filled membrane is formed generally according to the process as described by Jacoby U.S. Pat. No. 5,594,070 wherein a film of thickness greater than 0.005 mm and less than 2 mm, and more preferably 0.01 mm to 1.0 mm is formed from the following composition on a cast-film extrusion line at a temperature between 180°C and 275°C. The composition  
15      includes 100 parts by weight of polymeric resin, 40-90 parts by weight of which is an ethylene-propylene block copolymer having an ethylene content of 30-45% (available from Himont), 5-40 parts by weight of which is polypropylene homopolymer with a melt flow rate of 1-30 dg/min per ASTM D1238 (available from Amoco Chemical Company), 1-10 parts by weight of which is a low  
20      molecular weight polypropylene having a melt viscosity of 70-500 poise (available from Polyvisions Inc.). The composition additionally includes 0.5-10 ppm of red quinacridone dye beta-spherulite nucleating agent and 5-30 parts by weight of activated carbon having a mean particle diameter between 0.1  $\mu\text{m}$  and 10- $\mu\text{m}$ . The cast film is subsequently reheated to between 35°C and 140°C, and stretched either  
25      monoaxially or biaxially on a tenter frame at a stretch ratio of 1.5 to 10 to induce pore formation. The activated carbon filled membrane of this example can be formed and wound up on a roll for subsequent mono- or biaxial stretching, or can be stretched in-line during the film casting process.

30       The microporous, activated carbon filled membrane made according to this example can be further laminated to additional layers of similar or different

- microporous membranes or coatings, and/or to one or more layers of woven, nonwoven, or foamed fabrics. Examples of such fabrics include spunbonded fabrics, needled fabrics, hydro-entangled fabrics, powder-bonded fabrics, flashspun fabrics, carded webs, meltblown fabrics, self-bonded fabrics, cross-laminated fibrillated film fabrics, scrims, woven fabrics, knitted fabrics, as well as other woven and nonwoven fabrics. These fabrics can be constructed of one type of fibers or blends of different fibers, the fibers themselves of which can be bicomponent fibers. If desired these fabrics can be fabricated to have adsorptive properties, such as by using adsorbent coatings, impregnants, or adsorbent fibers.
- 5      10     These composites can be laminated together in various configurations of microporous membranes and fabrics to achieve the desired end performance characteristics according to various common laminating techniques including adhesive, extrusion, thermal, flame, solvent, and ultrasonics.

Membranes and composites made according to this invention can be employed in a wide range of applications requiring moisture vapor transmission, resistance to particulate penetration, resistance to chemical penetration and permeation, as well as characteristics of odor control. Anticipated applications include protective garments for protection against liquid and/or airborne contaminants, garments for preventing transmission of human body odor, such as hunting garments, garment inserts, gloves, glove inserts, shoe inserts, seam tape for taping the seams of protective garments, packaging materials, personal hygiene products, including infant diapers and adult incontinence products, feminine hygiene products, surgical gowns, drapes, and related items, building construction items including housewrap and roofing underlayment, outdoor covers, filters, liquid and gas separation membranes, battery separators, etc.

15     20     25

#### Example 2

- A microporous, activated carbon filled membrane is formed according to Example 1 with the addition of 100-2000 ppm of an antimicrobial additive such as 2,4,4'-trichloro-2'-hydroxydiphenyl ether (example of which is available as
- 30     Microban® from Clinitex Corp.).

### Example 3

Similar examples of microporous, activated carbon filled membranes can be formed generally according to the process described by Weimer et al. U.S. Pat. No. 5,690,949 with the addition of activated carbon. The polymeric composition 5 includes a processing compound such as a hydrocarbon liquid (i.e., mineral oil) that will dissolve in the polymer resin matrix and phase separate upon cooling and a fluorochemical additive to improve water and oil repellency. Here, the stretched film is annealed at between 100°C and 150°C after stretching. In this case, the activated carbon is suspended in the hydrocarbon liquid processing agent during 10 compounding, mixing, and extrusion (i.e., either cast or blown film) and remains in the micropores after stretching thus imparting adsorptive characteristics to the final film or membrane.

### Example 4

A microporous, activated carbon filled membrane is formed generally 15 according to the process described by Wu et al. U.S. Pat. No. 5,865,926 wherein a film of thickness greater than 0.25 mils and less than 10.0 mils, and more preferably 0.25 mils to 2.0 mils, is formed from a microporous formable, activated carbon filled resin that has been extrusion coated onto a .25 oz/yd<sup>2</sup> to 5 oz/yd<sup>2</sup> spunbonded polypropylene fabric (example of which is available from BBA 20 Nonwovens) and is subsequently stretched by passing the composite through a series of intermeshing rollers thus causing cavitation around the activated carbon and inducing breathability via a system of interconnected micropores. The microporous formable polymeric resin composition for this example is comprised 25 of 17-82% by weight of a polyolefin such as low density polyethylene, linear low density polyethylene, high density polyethylene, polypropylene, and copolymers such as ethylene vinyl acetate (EVA), ethylene methylacrylate (EMA) and ethylene acrylic acid (EAA), or blends thereof, 17-67% by weight of activated carbon having a mean particle diameter between 0.5µm and 8.0 µm and more preferably around 1µm, and 1-67 weight percent of a liquid or waxy hydrocarbon polymer 30 such as liquid polybutene, polybutadiene or hydrogenated liquid polybutadiene.

The microporous formable composition is extruded on common extrusion equipment at a melt temperature between 400°F and 500°F with a nip pressure between 10 and 80 psi. Alternatively a vacuum roller can be used in place of the nip roller to promote lamination of the microporous formable resin to the

5 nonwoven material. Incremental stretching is accomplished by preheating the microporous formable, activated carbon filled web to between 70°F and 90°F and passing it through intermeshing rollers that induce an incremental degree of stretch. Stretching can be either diagonally which induces both machine and transverse stretch, or alternatively, the web can be stretched by a set of transverse

10 intermeshing rollers, or a set of machine direction intermeshing rollers or a combination of such. The preferred intermeshing engagement is 0.06 inch to 0.12 inch to induce sufficient microporosity. Unlike the uniform microporosity of Example 1, this technique induces defined incremental microporosity thus leaving a portion of the composite non-porous, which can have unique application

15 especially in the area of permselective membranes.

#### Example 5

The microporous formable polymeric resin composition of Example 4 is extrusion cast as a free film. Subsequently, the free film is incrementally stretched as described in Example 4.

20

#### Example 6

A microporous activated carbon filled free film is formed according to Example 5. The unstretched membrane is laminated to a .25 oz/yd<sup>2</sup> to 5 oz/yd<sup>2</sup> spunbonded polypropylene fabric (an example of which is available from BBA Nonwovens) using a hot melt, aqueous, or solid based adhesive system. This 25 composite is subsequently incrementally stretched as described in Example 4.

#### Example 7

A microporous, activated carbon filled membrane is formed according to the cold draw process as described by Hoge U.S. Pat. No. 4,350,655 wherein a film of thickness greater than about 0.25 mils and less than about 10.0 mils, and more

preferably about 5.0 mils, is formed from a highly filled thermoplastic composition that is stretched via the cold draw process. The thermoplastic composition of the membrane contains between 30% and 50% by weight of one or more polymeric resins including high density polyethylene, polyethylene, low density polyethylene, 5 linear low density polyethylene, polypropylene, polyamide, polyester, or blends thereof, and 50% to 70% by weight of activated carbon having a mean particle diameter between 0.5  $\mu\text{m}$  and 10  $\mu\text{m}$  and more preferably between 1  $\mu\text{m}$  and 5  $\mu\text{m}$ . The activated carbon filled resin composition is extruded on common extrusion equipment at a temperature between 180°C and 400°C and then rapidly cooled to 10 10°C to 70°C to minimize any stretching of the hot web. The chilled web is then stretched monoaxially or biaxially using grooved rollers as common in the art to induce the desired level of microporosity. Stretching rates of <300 cm/sec inducing stretch ratios of between 2X and 5X are preferred. Variations in resin blends and stretch ratios can and do affect the final performance of the film. In a 15 variation of this example, the activated carbon filled composition is melt embossed during the casting process and prior to stretching to induce other characteristics to the final structure.

It should be evident that the present invention is applicable to other microporous film forming processes, its novelty being to induce "active" 20 adsorptive properties to otherwise "passive" microporous films and composites. It should be further noted that multiple layers of microporous films could be combined by themselves or with various fabrics according to known laminating techniques (i.e., thermal, adhesive, extrusion, ultrasonic, etc.) to produce a variety of performance characteristics. These composites can include both traditional 25 filled microporous films and activated carbon filled microporous films and coatings. The activated carbon filled films of which can also include other organic and inorganic mechanical pore forming agents and other additives.

Many modifications and other embodiments of the inventions set forth herein will come to mind to one skilled in the art to which these inventions pertain 30 having the benefit of the teachings presented in the foregoing descriptions and the associated drawings. Therefore, it is to be understood that the inventions are not to be limited to the specific embodiments disclosed and that modifications and other

embodiments are intended to be included within the scope of the appended claims. Although specific terms are employed herein, they are used in a generic and descriptive sense only and not for purposes of limitation.

**THAT WHICH IS CLAIMED IS:**

1. A microporous membrane comprising a polymeric resin material and an activated carbon filler material distributed throughout the membrane and functioning both as a mechanical pore-forming agent for rendering the membrane microporous and as a adsorbent.
2. The microporous membrane of Claim 1, wherein the activated carbon filler material has a mean particle diameter of less than 15 microns.
3. The microporous membrane of Claim 1, including organic and/or inorganic mechanical pore-forming agents in addition to said activated carbon filler material.
4. The microporous membrane of Claim 3, wherein the additional organic and/or inorganic mechanical pore-forming agent is at least one member selected from the group consisting of zeolites, clay, calcium carbonate, barium sulfate, magnesium carbonate, magnesium sulfate, alkaline earth metals, baking soda, activated alumina, silica, calcium oxide, soda lime, titanium dioxide, aluminum hydroxide, ferrous hydroxides, diatomaceous earths, borax, acetyl salicylic acid, molecular sieves, ion exchange resins, talc, kaolin, silica, magnesium carbonate, barium carbonate, calcium sulfate, zinc oxide, calcium oxide, mica, glass, wood pulp, and pulp powder.
5. The microporous membrane of Claim 3, wherein the additional organic and/or inorganic mechanical pore-forming agent has been further treated with surface modifiers to minimize agglomeration and improve dispersion.
6. The microporous membrane of Claim 1, wherein the activated carbon filler material has been further treated with surface modifiers to minimize agglomeration and improve dispersion.
7. The microporous membrane of Claim 1, wherein the polymeric resin material is selected from the group consisting of polyolefins, polyolefin

copolymers, polyesters, polyamides, polyvinyl alcohol, polycaprolactone, starch polymers, and blends thereof.

8. The microporous membrane of Claim 1, wherein the membrane is an unsupported film.

5 9. The microporous membrane of Claim 1, wherein the membrane is a coating supported by a flexible supporting substrate.

10. The microporous membrane of Claim 9, wherein the flexible supporting substrate is a nonwoven fabric.

11. The microporous membrane of Claim 1, that has been combined  
10 with one or more layers selected from the group consisting of woven fabric, nonwoven fabric and scrim.

12. The microporous membrane of Claim 1, that has been combined with a woven or nonwoven fabric layer that has adsorptive properties.

13. The microporous membrane of Claim 1, that has been combined  
15 with one or more additional microporous membrane layers.

14. The microporous membrane of Claim 13, wherein at least one of said additional microporous membrane layers comprises a polymeric resin material and a mechanical pore-forming agent selected from the group consisting of zeolites, clay, calcium carbonate, barium sulfate, magnesium carbonate, magnesium sulfate, alkaline earth metals, baking soda, activated alumina, silica, calcium oxide, soda lime, titanium dioxide, aluminum hydroxide, ferrous hydroxides, diatomaceous earths, borax, acetyl salicylic acid, molecular sieves, ion exchange resins, talc, kaolin, silica, magnesium carbonate, barium carbonate, calcium sulfate, zinc oxide, calcium oxide, mica, glass, wood pulp, and pulp powder.  
20

25 15. The microporous membrane of Claim 1, wherein the membrane has been treated with a hydrophobic agent.

16. The microporous membrane of Claim 1, in which there is also dispersed throughout the membrane at least one additive selected from the group consisting of flame retardants, anti-static additives, anti-microbial additives, antioxidants, stabilizers, UV absorbers, and enzyme additives.

5 17. The microporous membrane of Claim 1, wherein said activated carbonfiller material has a carbon tetrachloride adsorption activity of 50% or greater according to ASTM D3467.

18. A seam tape formed from the microporous membrane of Claim 1.

19. A garment including the microporous membrane of Claim 1 for odor  
10 control.

20. A personal hygiene product including the microporous membrane of Claim 1 for odor control.

21. A glove formed from the microporous membrane of Claim 1.

22. A filter formed from the microporous membrane of Claim 1.

15 23. A microporous composite sheet material comprising a plurality of superposed microporous membrane layers, wherein at least one of the membrane layers is a microporous membrane comprising a polymeric resin material and an activated carbon filler material distributed throughout the membrane and functioning both as a mechanical pore-forming agent for rendering the membrane  
20 microporous and as a adsorbent.

24. The microporous material of Claim 23, wherein at least one other layer of the microporous sheet material includes a mechanical pore-forming agent different from said activated carbon filler material.

25 25. The microporous material of Claim 24, wherein an exterior layer contains a mechanical pore-forming agent and an interior layer contains said activated carbon filler material.

26. The microporous material of Claim 25, wherein the mechanical pore-forming agent in the exterior layer is selected from the group consisting of zeolites, clay, calcium carbonate, barium sulfate, magnesium carbonate, magnesium sulfate, alkaline earth metals, baking soda, activated alumina, silica, calcium oxide, soda lime, titanium dioxide, aluminum hydroxide, ferrous hydroxides, diatomaceous earths, borax, acetyl salicylic acid, molecular sieves, ion exchange resins, talc, kaolin, silica, magnesium carbonate, barium carbonate, calcium sulfate, zinc oxide, calcium oxide, mica, glass, wood pulp, and pulp powder.
- 5
27. The microporous material of Claim 23, wherein said plurality of membrane layers comprises coextruded layers.
- 10
28. The microporous material of Claim 23, wherein said plurality of membrane layers comprise laminated preformed membrane layers.
- 15
29. The microporous material of Claim 23, which includes a nonwoven fabric supporting substrate, and wherein at least one of the microporous membrane layers is an extrusion coating overlying the nonwoven fabric supporting substrate.
- 20
30. A microporous composite sheet material having an outer surface and an inner surface and comprising a first microporous membrane layer comprising a polymeric resin material and an activated carbon filler material distributed throughout the membrane and functioning both as a mechanical pore-forming agent for rendering the membrane microporous and as an adsorbent, a second microporous membrane layer comprising a polymeric resin material and a mechanical pore forming agent different from said activated carbon filler material, said second microporous membrane layer being located closer to said outer surface than the first microporous membrane layer, and at least one reinforcing layer selected from the group consisting of woven fabrics, knitted fabrics, nonwoven fabrics, and scrims.
- 25
31. A method of producing a microporous adsorbent membrane, which comprises: forming a membrane including a polymeric resin material and an activated carbon filler material distributed throughout the membrane and

functioning both as a mechanical pore-forming agent for rendering the membrane microporous and as an adsorbent, and stretching the membrane to render it microporous.

32. The method of Claim 31, wherein the step of forming a membrane  
5 comprises forming a membrane which includes an organic and/or inorganic  
mechanical pore-forming agent in addition to said activated carbon filler material.

33. The method of Claim 32, wherein the additional organic and/or  
inorganic mechanical pore-forming agent is selected from the group consisting of  
zeolites, clay, calcium carbonate, barium sulfate, magnesium carbonate,  
10 magnesium sulfate, alkaline earth metals, baking soda, activated alumina, silica,  
calcium oxide, soda lime, titanium dioxide, aluminum hydroxide, ferrous  
hydroxides, diatomaceous earths, borax, acetyl salicylic acid, molecular sieves, ion  
exchange resins, talc, kaolin, silica, magnesium carbonate, barium carbonate,  
calcium sulfate, zinc oxide, calcium oxide, mica, glass, wood pulp, pulp powder,  
15 and mixtures of the foregoing.

34. The method of Claim 31, wherein the polymeric resin material is  
selected from the group consisting of polyolefins, polyolefin copolymers,  
polyesters, polyamides, polyvinyl alcohol, polycaprolactone, starch polymers,  
blends thereof.

20 35. The method of Claim 31, including treating the membrane with a  
hydrophobic agent to enhance hydrophobicity.

36. The method of Claim 31, wherein the step of forming a membrane  
comprises forming the membrane as an unsupported film.

25 37. The method of Claim 31, wherein the step of forming a membrane  
comprises forming the membrane as a coating on a flexible supporting substrate.

38. The method of Claim 31, including forming an additional microporous membrane and combining the additional membrane with said adsorbent microporous membrane to form a microporous multi-layer composite.

39. The method of Claim 38, wherein the microporous multi-layer  
5 composite has an exterior layer and an inner layer, and wherein the exterior layer contains a mechanical pore-forming agent and the interior layer contains said adsorptive pore-forming agent.

40. The method of Claim 39, wherein the mechanical pore-forming agent is selected from the group consisting of zeolites, clay, calcium carbonate,  
10 barium sulfate, magnesium carbonate, magnesium sulfate, alkaline earth metals, baking soda, activated alumina, silica, calcium oxide, soda lime, titanium dioxide, aluminum hydroxide, ferrous hydroxides, diatomaceous earths, borax, acetyl salicylic acid, molecular sieves, ion exchange resins, talc, kaolin, silica, magnesium carbonate, barium carbonate, calcium sulfate, zinc oxide, calcium oxide, mica, glass, wood pulp, and pulp powder, and mixtures of the foregoing.  
15

41. The method of Claim 40, including treating the mechanical pore forming agent to improve its adsorptive specificity and or capacity.

42. The method of Claim 38, wherein the multi layered composite is formed in-line by extruding successive membrane layers from respective dies.

20 43. The method of Claim 38, wherein the multi layered composite is formed by coextruding the respective membrane layers from a coextrusion die.

44. The method of Claim 38, wherein the multi layered composite is by laminating preformed membrane layers thermally, adhesively, or ultrasonically.

25 45. The method of Claim 38, wherein one or more layers of the multi layered composite is formed by extrusion coating.

46. The method of Claim 31, including laminating the microporous membrane to one or more layers of woven or nonwoven fabric.

47. The method of Claim 31, including laminating the microporous membrane to one or more layers of strength enhancing scrim.

48. The method of Claim 31, including also dispersing throughout the membrane at least one additive selected from the group consisting of flame retardants, anti-static additives, anti-microbial additives, and enzyme additives.

49. The method of Claim 31, including also dispersing throughout the membrane a starch additive to promote degradation of the membrane when exposed to sunlight.

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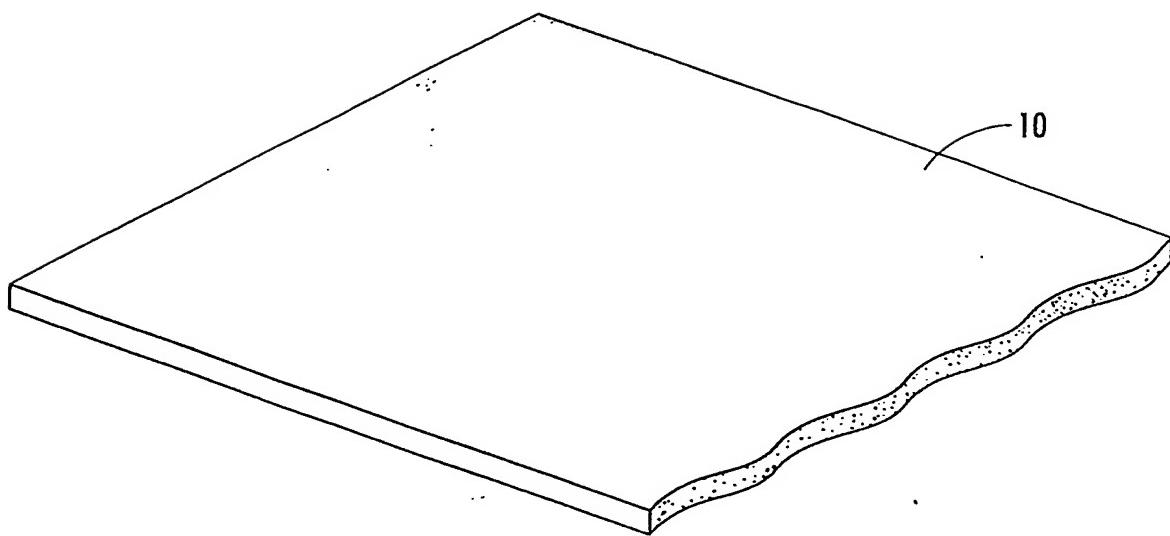


FIG. 1

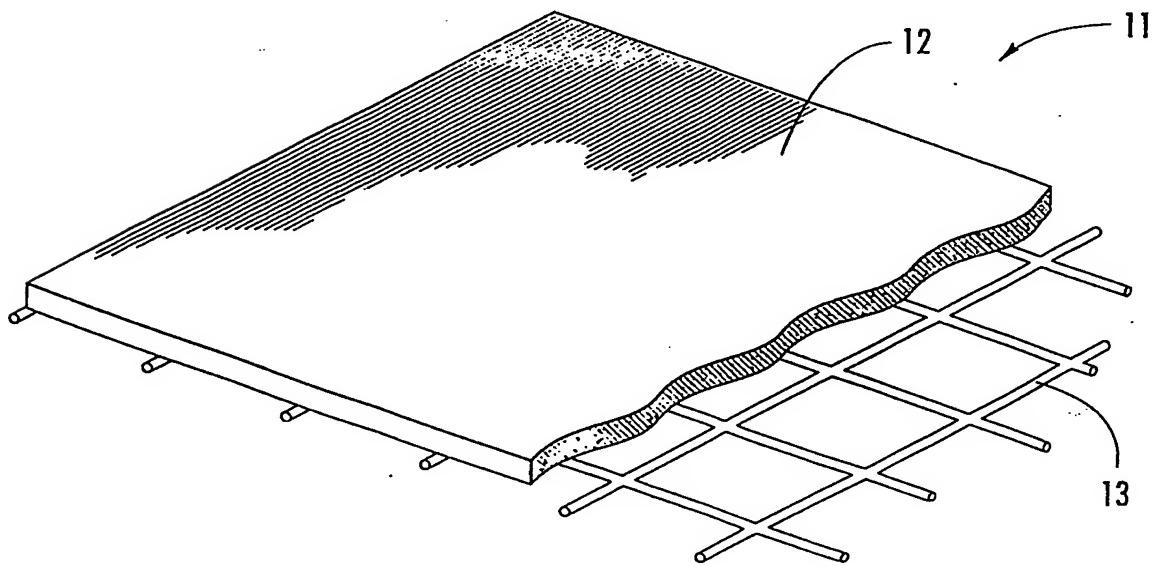


FIG. 2

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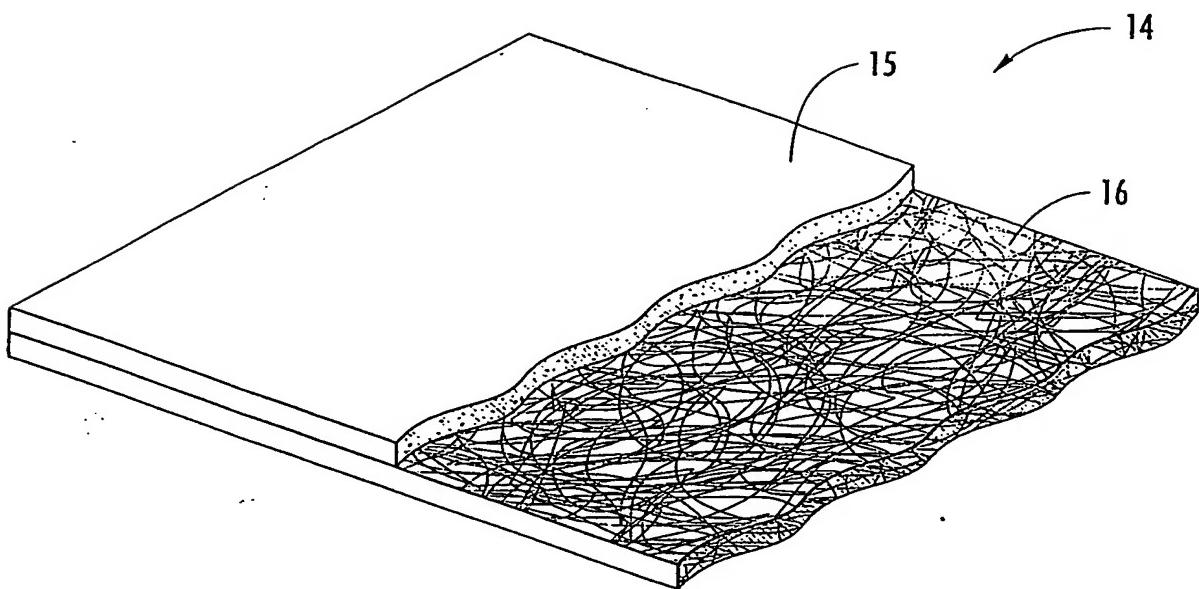


FIG. 3

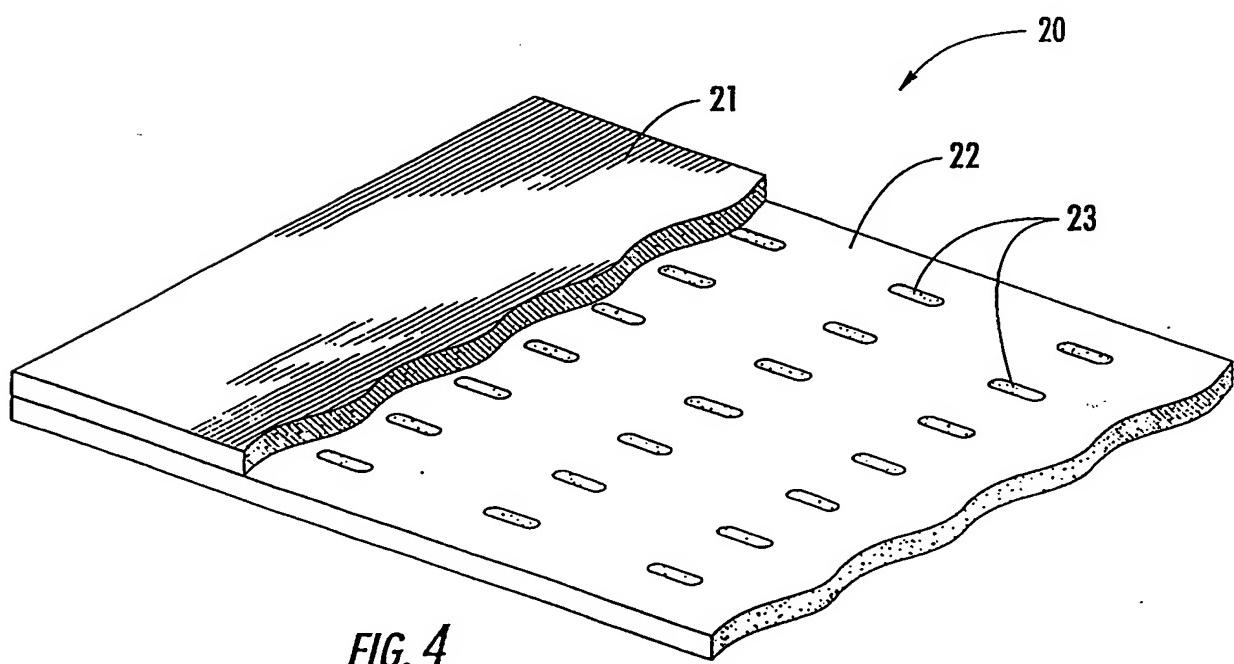


FIG. 4

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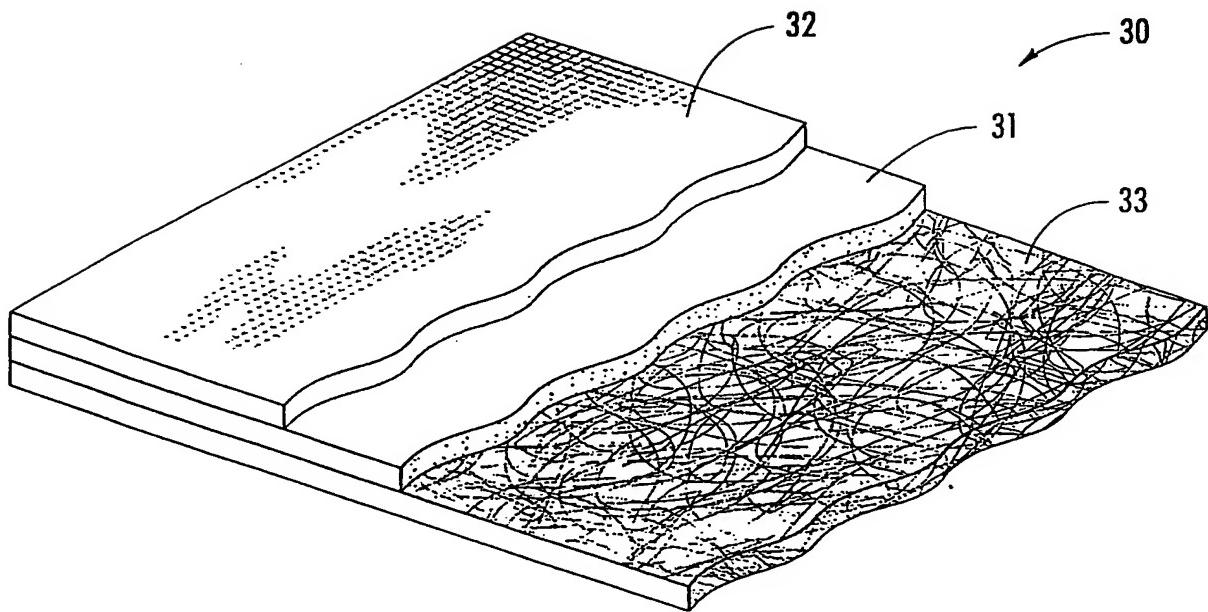


FIG. 5

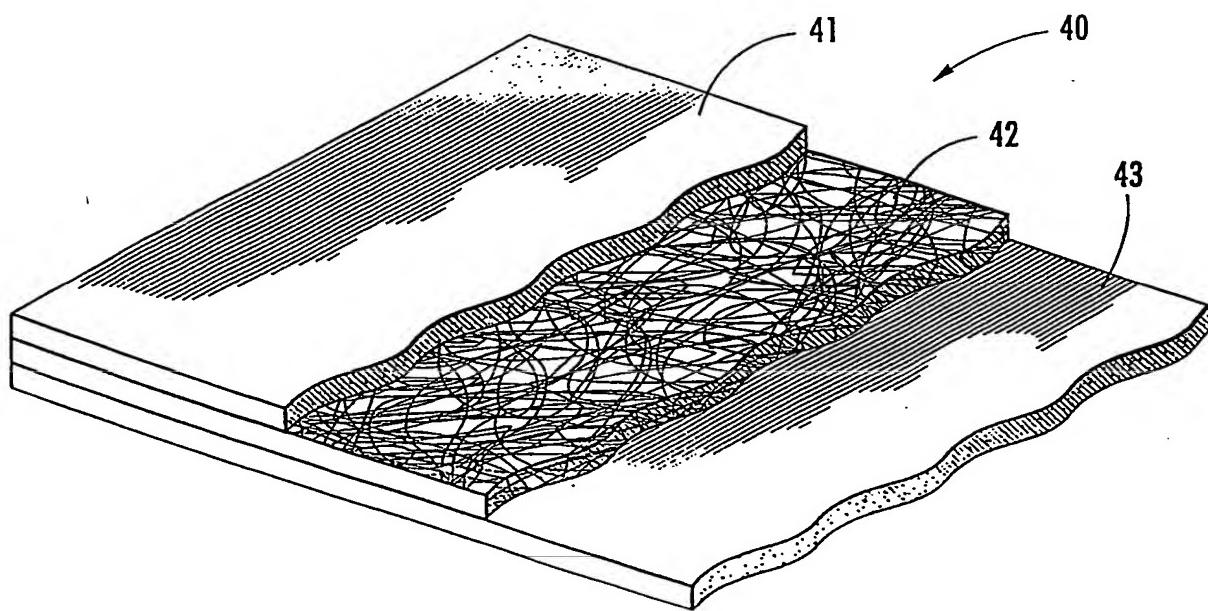


FIG. 6

## INTERNATIONAL SEARCH REPORT

Inte  
onal Application No  
PCT/US 03/18404

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C08J5/18 C08J5/22 B32B5/32 B32B5/18

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C08J B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Derwent Publications Ltd., London, GB; AN 1991-213038 XP002253281 & JP 03 136837 A (NITTO DENKO CORP), 11 June 1991 (1991-06-11) abstract — PATENT ABSTRACTS OF JAPAN vol. 011, no. 394 (C-465), 23 December 1987 (1987-12-23) & JP 62 153324 A (DAINIPPON PRINTING CO LTD), 8 July 1987 (1987-07-08) abstract — —/—	1-49
X		1-49

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
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- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the International filing date but later than the priority date claimed

- \*T\* later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the International search

3 September 2003

Date of mailing of the International search report

19/09/2003

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## INTERNATIONAL SEARCH REPORT

Int'l Application No  
PCT/US 03/18404

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 1988-171493 XP002253296 & JP 63 109046 A ( DAIICHI LACE KK;TORAY IND INC ), 13 May 1988 (1988-05-13) abstract ---	1-49
X	EP 0 380 353 A (MITSUBISHI CHEM IND) 1 August 1990 (1990-08-01) page 2, line 1-55 page 5, line 19 -page 6, line 51 ---	1-12
X	PATENT ABSTRACTS OF JAPAN vol. 1996, no. 01, 31 January 1996 (1996-01-31) & JP 07 232042 A (TOKUYAMA CORP), 5 September 1995 (1995-09-05) abstract ---	1-12
X	DATABASE WPI Derwent Publications Ltd., London, GB; AN 1976-27057X XP002253282 & JP 51 022765 A (MATSUSHITA ELEC IND CO LTD), 23 February 1976 (1976-02-23) abstract ---	1-12
X	EP 0 212 572 A (ELNA CO LTD ;ASAHI GLASS CO LTD (JP)) 4 March 1987 (1987-03-04) column 1, line 1-5 column 3, line 10- -column 5, line 42; claims; examples ---	1,2

## INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte

nal Application No

PCT/US 03/18404

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
JP 3136837	A	11-06-1991	NONE			
JP 62153324	A	08-07-1987	NONE			
JP 63109046	A	13-05-1988	NONE			
EP 0380353	A	01-08-1990		JP 2199135 A JP 2621456 B2 JP 2309969 A JP 2797434 B2 CA 2008625 A1 DE 69012358 D1 DE 69012358 T2 EP 0380353 A2 ES 2062326 T3 JP 2276834 A JP 2859346 B2 KR 147284 B1 US 5015521 A		07-08-1990 18-06-1997 25-12-1990 17-09-1998 27-07-1990 20-10-1994 09-03-1995 01-08-1990 16-12-1994 13-11-1990 17-02-1999 17-08-1998 14-05-1991
JP 07232042	A	05-09-1995	NONE			
JP 51022765	A	23-02-1976	NONE			
EP 0212572	A	04-03-1987		DE 3680163 D1 EP 0212572 A2 JP 2065479 C JP 7105316 B JP 63107011 A US 4862328 A		14-08-1991 04-03-1987 24-06-1996 13-11-1995 12-05-1988 29-08-1989